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FORMATION OF ALKYL RADICALS THAT ARE RELATIVELY UNREACTIVE WITH EACH OTHER AND WITH OXYGEN, IN THE LOW-TEMPERATURE LIQUID-PHASE OXIDATION OF HEXAFLUOROPROPYLENE BY MOLECULAR OXYGEN

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Kinetic evidence has been found for the participation of stable alkyl radicals in the reaction of low-temperature liquid-phase oxidation of hexafluoropropylene by molecular oxygen. The presence of such stable radicals is proven by the nonparticipation of alkyl radicals in chain-breaking, and also by the formation of epoxide at significant rates when the oxygen pressure is high.

In the work of Allarov, Barkalov, et al. on the radiolysis of hexafluoropropylene (HFP) and other fluorocarbons by ^{60}Co γ-radiation (see for example [1-3]), they detected alkyl radicals that are stable in the liquid phase, with an abnormally long lifetimes (100-1000 h) at room temperature, even in the presence of oxygen.

It was also found that in the low-temperature liquid-phase oxidation of HFP by molecular oxygen, kinetic evidence can be found for participation in the process by alkyl radicals that are relatively unreactive in their reactions with each other (chain breaking) and with oxygen.

The products from the oxidation of HFP are perfluoropolyetherpolyperoxide (PFPP), which is a liquid oligomer with molecular weight 10^3-10^4, along with HFP oxide C_3F_6O, trifluoroacetyl fluoride CF_3COF, and carbonyl fluoride COF_2. In the structure of the PFPP, more than 90% of the units are ether units, mainly —C_3F_6O—. There are also —$CF(CF_3)O$— and —CF_2O— units [4]. The mechanism of PFPP formation is as follows [4, 5]:

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \quad (I)$$

$$RO_2^{\cdot} + C_3F_6 \rightarrow RO_2C_3F_6^{\cdot}\ (R^{\cdot}) \quad (II)$$

$$RO_2^{\cdot} + RO_2^{\cdot} \rightarrow 2RO^{\cdot} + O_2 \quad (III)$$

$$RO^{\cdot} + C_3F_6 \rightarrow ROC_3F_6^{\cdot}\ (R^{\cdot}) \quad (IV)$$

The HFP oxide is formed mainly in the reaction of fragmentation of alkyl radicals in which the last oxygen link is an ether [6]:

$$ROC_3F_6^{\cdot} \rightarrow R^{\cdot} + C_3F_6O \quad (V)$$

The most probable mechanism of formation of low-molecular-weight acid fluorides is an abnormal variant of the nonterminated interaction of peroxide radicals [7]:

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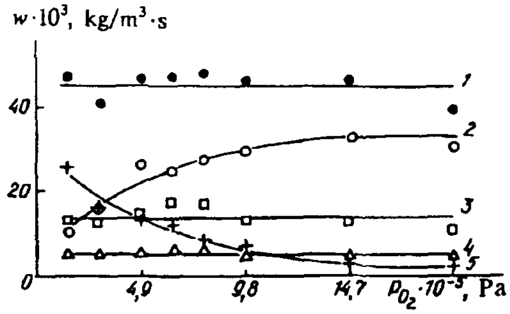

Fig. 1. Rates of HFP consumption and product formation as functions of oxygen pressure: *1*) HFP; *2*) PFPP; *3*) trifluoroacetyl fluoride; *4*) carbonyl fluoride; *5*) HFP oxide.

$$RO_2^{\cdot} + ROCF_2CF(CF_3)O_2^{\cdot} \rightarrow RO^{\cdot} + O_2 + ROCF_2^{\cdot}\,(R^{\cdot}) + CF_3COF \quad \text{(VIa)}$$

$$RO_2^{\cdot} + ROCF(CF_3)CF_2O_2^{\cdot} \rightarrow RO^{\cdot} + O_2 + ROCF(CF_3)^{\cdot}(R^{\cdot}) + COF_2 \quad \text{(VIb)}$$

In our experiments, the HFP oxidation was performed in a 150-cm^3 stainless steel reactor. The perfluoroolefin charge was 50 g. Oxygen was fed to the reactor through a drying system. The reaction mixture was agitated by a magnetic stirrer. The gaseous components were analyzed chromatographically [8]. The content of peroxide oxygen in the PFPP was determined iodometrically [4]. The reaction was initiated by ^{60}Co γ-radiation with an absorbed dose rate of 0.9 Gy/s.

In Fig. 1 we have plotted the rates of HFP consumption and product formation as functions of oxygen pressure, at 303 K. It can be seen from these results that the rate of HFP consumption is independent of the oxygen pressure; this reflects nonparticipation of alkyl radicals in chain-breaking [8]. We also observed formation of the epoxide at a significant rate, even with an oxygen pressure of $19.6 \cdot 10^5$ Pa. This indicates that even under such conditions, an adequate stationary concentration of alkyl radicals will exist, and competition with the reaction direction (I) cannot completely suppress reaction (V). By way of comparison, consider the reaction of styrene oxidation [5], where epoxidation is almost completely suppressed even with an oxygen pressure of 40-50 mm Hg.

Thus, the low reactivity of alkyl radicals in their reactions with each other and with oxygen leaves its mark on the kinetics of low-temperature liquid-phase oxidation of HFP.

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